Evidence for Local Moment by Electron Spin Resonance Study on Polycrystalline $LaFeAsO_{1-x}F_x$ (x=0 and 0.13)

T. Wu, J. J. Ying, G. Wu, R. H. Liu, Y. He, H. Chen, X. F. Wang, Y. L. Xie, Y. J. Yan and X. H. Chen*
Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

The temperature dependence of electron spin resonance (ESR) was studied in the oxypnictide superconductors $LaFeAsO_{1-x}F_x$ (x = 0.0 and 0.13). In the samples, the ESR signal indicates that the g factor and peak-to-peak linewidth strongly depend on temperature, especially at low temperatures. It indicates a strong coupling picture with existence of local moment. The dependence mentioned above gradually attenuates, and tends to saturation around room-temperature. This behavior could be ascribed to "bottleneck" effect due to coupling of local moment and itinerant electron. In addition, a Curie-Weiss like behavior is also observed in temperature dependent integral intensity for the two samples. Our results strongly support the existence of local moments in these materials while its origin is still unclear. The results also indicate strong magnetic frustration in this system, and magnetic fluctuation mechanism for superconductivity is suggested.

PACS numbers: 31.30.Gs,71.38.-k,75.30.-m

The discovery of Fe-based high Tc superconductor provides a new materials base to explore the mechanism of high-Tc superconductivity besides high-Tc cuprates superconductor[1,2,3,4,5]. Similar to cuprates, Such pnictide superconductors are also believed to have a quasi-2D conducting layer—Fe_2As_2 layer, which is separated by LnO (Ln = La, Sm etc.) or R (R = Ba, Sr etc.) charge reservior. With doping electron or hole, the ground state of FeAs compounds evolves from spin-density-wave state (SDW) to superconducting state (SC). Electronic phase diagrams of FeAs compounds were also found to be similar to the high-Tc cuprates[1,6,7,8,9,10,11], where strong electron-electron coupling is believed to be the key to understand high-Tc superconductivity. Therefore, one may naturally ask whether it is still the case in iron-pnictides. As we know, strong in-site Coulomb interaction can produce local moment in cuprates. The existence of local moment is believed to be a strong evidence for strong coupling. In FeAs parent compounds, the magnetic moment of Fe^{2+} ion is theoretically predicted to be 2.4 - 2.6 μ_B[12,13,14] while neutron results show a smaller magnetic moment about 0.36-0.87μ_B[9,15,16,17,18]. Moreover, the static susceptibilities for parent compounds decrease with decreasing temperature and shows a linear-temperature behavior above SDW transition[19,20,21]. These results challenge the strong coupling picture. In this paper, we *firstly* studied temperature dependence of electron spin resonance (ESR) for $LaFeAsO_{1-x}F_x$ (x = 0.0 and 0.13). The benefit of ESR is that it can give us dynamic magnetic information of local moment. An intrinsic resonance signal was observed, and the g-factor and peak-to-peak linewidth show strong temperature-dependence in low temperature region for the samples. It indicates the existence of local moment, being consistent with strong coupling picture. Further, "Bottleneck" effect due to coupling between local moments and itinerant electrons was also observed in high temperature region. In addition, a Curie-Weiss like behavior in temperature dependent integral intensity was observed. These results strongly support the strong coupling picture.

Polycrystalline samples with nominal composition $LaFeAsO_{1-x}F_x$ (x = 0, 0.13) were synthesized by conventional solid state reaction using high purity LaAs, LaF_3, Fe and Fe_2O_3 as starting materials. LaAs was obtained by reacting La chips and As pieces at 600 ^oC for 3 hours and then 900 ^oC for 5 hours. The raw materials were thoroughly grounded and pressed into pellets. The pellets were wrapped up by Ta foil and sealed in an evacuated quartz tube. They were then annealed at 1160 ^oC for 40 hours. The sample preparation process except for annealing was carried out in glove box in which high pure argon atmosphere is filled. The XRD results show that the samples with x=0 is single phase. A tiny but noticeable trace of impurity phase LaOF was observed in x=0.13. The ESR measurements of the powder samples were performed using a Bruker ER-200D-SRC spectrometer, operating at X-band frequencies (9.47 GHz) and between 110 and 350 K. The resistance was measured by an AC resistance bridge (LR-700, Linear Research). Magnetic susceptibility measurements were performed with a superconducting quantum interference device magnetometer in a magnetic field of 7 T. It should be addressed that all results discussed as follow are well reproducible.

Fig.1 shows the temperature dependence of resistivity and magnetization for $LaFeAsO_{1-x}F_x$ with x = 0 and 0.13. For parent compound LaFeAsO, temperature dependence of resistivity shows a peak around 155 K due to structural transition, and the magnetization also shows a kink and at the same temperature as reported previously[1]. For F-doped sample, superconductivity with

*Corresponding author; Electronic address: chenxh@ustc.edu.cn

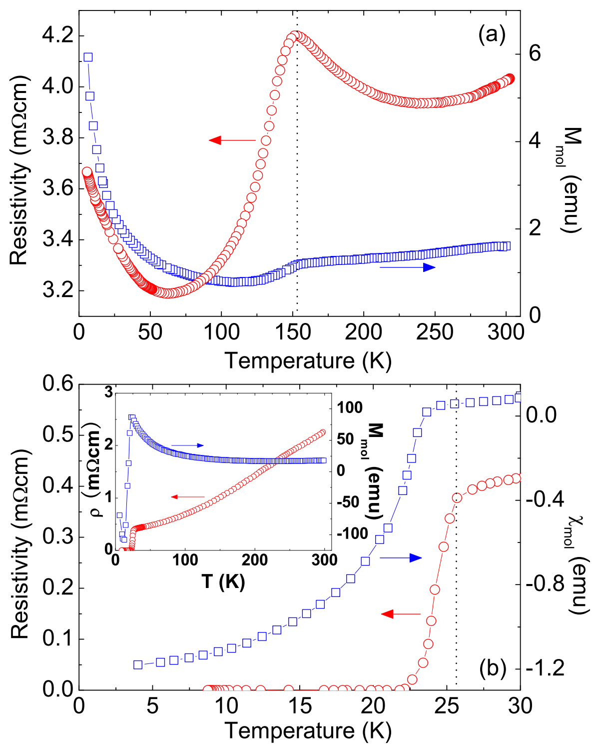

FIG. 1: (Color online). Temperature dependence of resistivity and magnetization for $LaFeAsO_{1-x}F_x$ (a) x = 0.0 and (b) x = 0.13. Magnetization in (a) and inset of (b) are measured with H = 1 T and susceptibility in (b) is measured with H = 10 Oe.

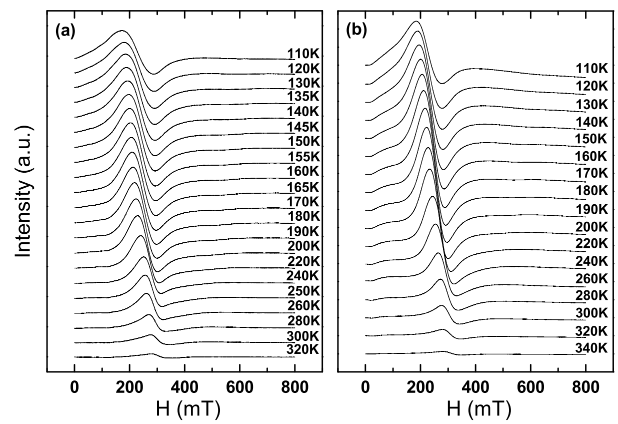

FIG. 2: ESR spectrum under different temperature for (a) x = 0.0 and (b) x = 0.13.

T_c = 26 K was observed in resistivity and magnetization as shown in Fig.1. These results show that the electric and magnetic properties of samples used here is consistent with previous works[1], indicating a good starting for the ESR study.

Temperature dependences of ESR spectra for x = 0 and 0.13 samples in the temperature range from 110 K to 350 K are shown in Fig.2. A tiny background from secondary phase (eg. FeAs) in samples was subtracted from the ESR spectra. A well-defined paramagnetic signal was observed for the x = 0 and x = 0.13 samples. Lorentz formula was used to fit the resonance signal very well. As shown in Fig.2, the linewidth is broadened and the resonance field shifts to the lower end with decreasing temperature. In traditional metal, no obvious paramagnetic resonance signal is expected due to rapid spin-lattice relaxation[32,33]. The observed resonance here should be considered to arise from local moment. In addition, we have tested the possible effect from the impurities. Such paramagnetic resonance signal was absent for all impurities at room temperature. It proves that the observed signal is intrinsic for this system.

Fig.3 shows temperature dependence of g factor and peak-to-peak linewidth ($\triangle H_{pp}$) for x = 0 and 0.13 samples. $\triangle H_{pp}$ is defined as the width between the highest point and the lowest point in temperature dependent ESR spectrum. The resonance field (H_c) to calculate g factor is defined as the magnetic field corresponding to the midpoint between the highest point and the lowest point in the ESR spectrum. The g factor is calculated by following formula: $g = \frac{h\nu}{\mu_B H_c}$. For the parent compound, the g factor monotonously increases with decreasing temperature below 300 K where a linear fitting works well. When temperature exceeds 300 K, g-factor is saturated. In Fig.3(b), g factor of F-doped sample shows a similar behavior. Compared to the parent compound, a more clear trend of g-factor saturation is presented above 260 K for the F-doped sample. Temperature dependent $\triangle H_{pp}$ also shows a similar behavior for the two samples. An upturn-behavior appears below 250 K for x = 0 sample and 200 K for x = 0.13 sample, respectively. Above the upturn-temperature, the $\triangle H_{pp}$ is saturated with increasing temperature in the two samples. The amplitude of $\triangle H_{pp}$ for x = 0 is almost the same as that of x = 0.13 sample above upturn temperature, and becomes larger below upturn temperature. It should be emphasized that the strong temperature dependence of g factor and $\triangle H_{pp}$ cannot be accounted for paramagnetic local moment because g_{eff} ($=g_s+\triangle g$) is temperature-independent, while linewidth $1/\tau$ (=a+bT) follows temperature-linear behavior for the system with paramagnetic local moment. Strong temperature-dependent g factor and $\triangle H_{pp}$ observed in ESR spectrum here has been explained by magnetic fluctuation in the system with magnetic phase transition[32,33]. It suggests that magnetic fluctuation from local moments exists in $LaFeAsO_{1-x}F_x$ (x = 0.0 and 0.13) system. Therefore, the question is naturally proposed: How to understand the origin of local moment? One possible explanation is that local spins from defects in FeAs layer lead to paramagnetic resonance ob-

served above. As shown in DC magnetization, a Curie tail behavior is observed in the low temperature for parent compound. By fitting the data with Curie-weiss formula, it is found that the number of S = 1/2 local spin is about ∼ 0.02 per Fe site and the Curie-weiss temperature is about ∼ 4 K. In this situation, a very weak intensity of paramagnetic resonance is expected at room temperature because the intensity is proportional to DC magnetization from local spin (about ∼ 0.02 per Fe site). Such expectation is in sharp contrast to the above observation. In addition, g-factor is much larger than 2 as in free electron's case as shown in Fig.3. Therefore, it indicates that the local spin from defects can be ruled out, and the local moment should come from Fe atom. But the magnetic state of Fe is still unclear. If local moments exist in a metal, a so-called "bottleneck" effect takes place in the transfer energy between the spin subsystem[32,33]. Figure 4 shows a cartoon picture for understanding "bottleneck" effect. τ_{se} and τ_{es} are relaxation times between local moments and itinerated electrons, respectively. τ_{el} is spin-lattice relaxation time for itinerated electrons. τ_{sl} is spin-lattice relaxation time for local moments. Usually, the local spins are adiabatic for lattice and the corresponding relaxation path is closed for local moments. When $\tau_{se} > \tau_{el}$, the magnetic energy of local moment can efficiently be passed on to lattice by itinerated electron, and the effective relaxation of local moments is determined by relaxation time τ_{se}. When $\tau_{se} < \tau_{el}$, magnetic energy of local moment, which is transferred to itinerated electron, is quite likely to be returned back rather than passed on to the lattice. Consequently, the relaxation process of the system is dominated by slow relaxation τ_{el}. The latter is called "bottleneck" effect. This effect is successfully used to explain the peculiar ESR features in $La_{1-x}Ca_xMnO_3$ and $La_{2-x}Sr_xCuO_4$ system in which local moments and itinerated electrons come from the same atoms[34,35]. The "bottleneck" effect is also expected in our system and can be used to understand high-temperature behavior of g factor and $\triangle H_{pp}$. The saturation of g factor and $\triangle H_{pp}$ with increasing temperature indicates that "bottleneck" effect gradually dominates with increasing temperature, which is similar to the observed results in $La_{1-x}Ca_xMnO_3$ and $La_{2-x}Sr_xCuO_4$[34,35]. Since the intensity of ESR signal decreases to the limit of the apparatus at high temperatures, a more clear evidence of "bottleneck" effect is lack in high temperature. But an increasing $\triangle H_{pp}$ and almost invariable g factor are expected, which are observed in many "bottleneck" system[34,35]. At low temperatures, the strong ferromagnetic fluctuation (g≫2) frustrates the relaxation between local moments and itinerated electrons and makes corresponding relaxation slowing down. With decreasing temperature, "bottleneck" effect is broken and a strong ferromagnetic fluctuation between local moments enhances the g factor and $\triangle H_{pp}$. These results show that there exists a ferromagnetic fluctuation from local moments. However, an antiferrmagnetic order is established below 135 K. It seems that dynamic magnetic properties observed here are very different from static magnetic properties.

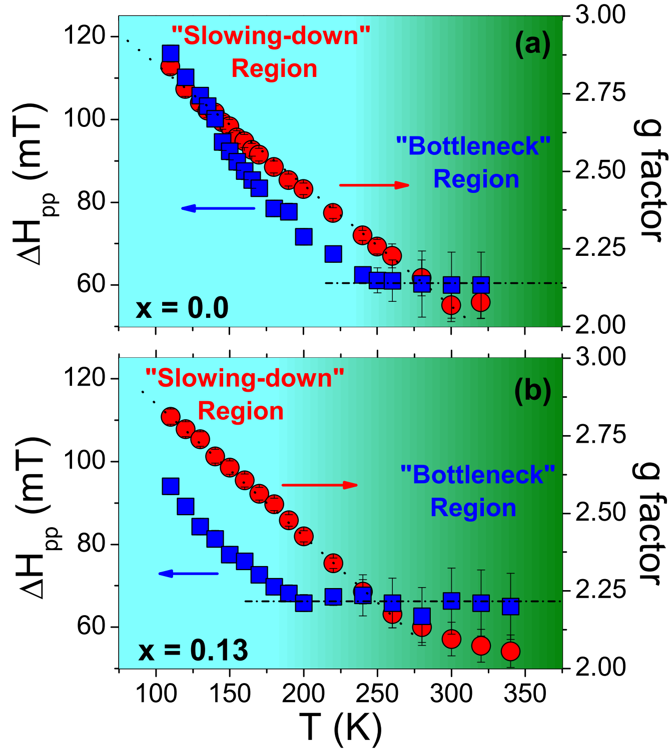

FIG. 3: (color online). Temperature dependence of g factor and $\triangle H_{pp}$ for (a) x = 0.0 and (b) x = 0.13.

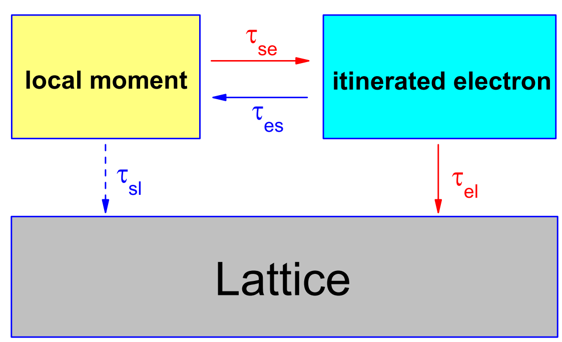

FIG. 4: (color online). Cartoon model for ESR "bottleneck" effect showing the various relaxation paths.

Fig.5 shows the temperature dependence of integral intensity of ESR spectrum for both x = 0 and 0.13 samples. For x = 0 sample, a Curie-weiss like behavior was observed for high temperature region and a kink is ob-

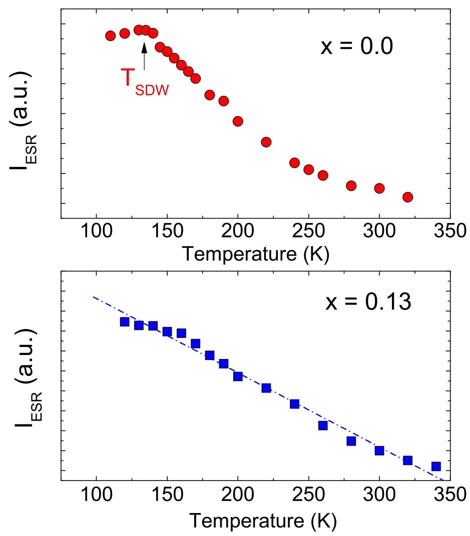

FIG. 5: (color online). Temperature dependence of integrated intensity. Top panel: x = 0.0; Bottom panel: x = 0.13.

served around 135 K which corresponds to the temperature of spin density wave transition determined by neutron scattering. Below 135 K, the intensity of x=0 sample decreases with decreasing temperature due to antiferromagnetic transition. For F-doped superconducting sample, Curie-weiss like behavior is weaken and a linear behavior is observed due to $I_{ESR} \propto \chi_{ESR}$[32,33]. Therefore, this result is also consistent with local moments picture.

Recently, the origin of magnetic order in FeAs superconductors is a very hot issue. Two distinct classes of theories have been proposed: local moment antiferromagnetic ground state for strong coupling[13,22,23,24,25,26] and itinerant ground state for weak coupling[27,28,29,30,31]. The local moment magnetism approach stresses on-site correlations, and assumes that the system is proximity to a Mott insulating state and the resemblance to cuprates; while the latter approach emphasizes the itinerated electron physics and the interplay between the competing ferromagentic and antiferromagnetic fluctuation. The observed results here may shed light on this debate. First, a "local moment" effect is observed. "Bottleneck" effect, Curie-weiss like behavior for χ_{ESR} and strong temperature dependence of g factor and $\triangle H_{pp}$ strongly support the existence of local moments. Secondly, ferromagnetic fluctuation is observed among local moments. Our results seem to favor strong coupling picture. But it is very strange that there exists a ferromagnetic fluctuation among local moments above the temperature of antiferromagnetic ordering. Kohama et al. observed a large Wilson ratio in $LaFeAsO_{1-x}F_x$, indicating ferromagnetic fluctuation in this system[36]. Recently, Zhang et al. proposed a "performed SDW moment scenario" to explain the temperature-linear behavior in DC magnetization[37]. It results from the existence of a wide fluctuation window in which the local spin-density-wave correlation exists but the global directional order has not yet been established. The so-called local moment is defined as performed SDW moment in this model. If we follow above idea, the observed ferromagnetic coupling could be understand in the way that there exists a wide ferromagnetic fluctuation window and it coexists and competes with antiferromagnetic fluctuation. Therefore, strong magnetic frustration maybe hidden in this system. Although the $\triangle H_{pp}$ decreases with F-doping, a similar behavior of g factor and $\triangle H_{pp}$ is observed in parent compound and F-doped superconducting compound, and it indicates that strong magnetic frustration is present in superconducting sample and magnetic fluctuation may be very important to understand superconductivity in this material. Similar result is also obtained in DC magnetization for polycrystalline $LaFeAsO_{1-x}F_x$[21].

In conclusion, we study temperature dependence of electron spin resonance (ESR) for $LaFeAsO_{1-x}F_x$ (x = 0.0 and 0.13). Strong temperature dependent g factor and $\triangle H_{pp}$ are observed at low temperatures for the samples. Curie-weiss like behavior is observed in the temperature dependent integral intensity. These results strongly support the existence of local moments in these materials, but its origin is still unclear (eg. "performed SDW moment"). Strong magnetic frustration exists in both the parent compound and superconducting sample. Magnetic fluctuation plays an important role in mechanism for superconductivity.

This work is supported by the Nature Science Foundation of China and by the Ministry of Science and Technology of China (973 project No: 2006CB601001) and by National Basic Research Program of China (2006CB922005).

[1] Y. Kamihara et al., *J. Am. Chem. Sco.* **130**, 3296(2008).
[2] X. H. Chen et al., Nature **453**, 761(2008).
[3] G. F. Chen et al., Phys. Rev. Lett. **100**, 247002(2008).
[4] Z. A. Ren et al., Europhys. Lett. **83**, 17002(2008).
[5] M. Rotter, M. Tegel, D. Johrendt, Phys. Rev. Lett. **101**, 107006(2008).
[6] J. Dong et al., Europhys. Lett., **83**, 27006(2008).
[7] R. H. Liu et al., Phys. Rev. Lett. **101**, 087001(2008).
[8] H. Luetkens et al. arXiv:0806.3533(2008).
[9] J. Zhao et al., arXiv:0806.2528(2008).
[10] A. J. Drew et al., arXiv:0807.4876(2008).
[11] H. Chen et al., arXiv:0807.3950v1(2008).
[12] F. J. Ma, Z. Y. Lu, Phys. Rev. B **78**, 033111(2008).
[13] C. Cao, P. J. Hirschfeld, H. P. Cheng, Phys. Rev. B **77**, 220506(R)(2008).
[14] F. J. Ma, Z. Y. Lu, T. Xiang, arXiv:0806.3526v1(2008).
[15] C. Cruz et al., Nature **453**, 899(2008).
[16] Q. Huang et al., arXiv:0806.2776v2(2008).
[17] Y. Qiu et al., arXiv:0806.2195(2008).
[18] Jun Zhao, Q. Huang, Clarina de la Cruz, J. W. Lynn, M.

D. Lumsden, Z. A. Ren, Jie Yang, Xiaolin Shen, Xiaoli Dong, Zhongxian Zhao, Pengcheng Dai, Phys. Rev. B **78**, 132504(2008).

[19] X. F. Wang et al., arXiv:0806.2452(2008).

[20] G. Wu et al., J. Phys.: Condens. Matter **20**, 422201(2008).

[21] R. Klingeler, N. Leps, I. Hellmann, A. Popa, C. Hess, A. Kondrat, J. Hamann-Borrero, G. Behr, V. Kataev, and B. B*ü*chner, arXiv:0808.0708v1(2008).

[22] K. Haule, J. H. Shim, G. Kotliar, Phys. Rev. Lett. **100**, 226402(2008).

[23] Z. P. Yin et al., Phys. Rev. Lett. **101**, 047001(2008).

[24] F. Ma et al., arXiv:0804.3370(2008).

[25] C. Fang, H. Yao, W. F. Tsai, J. P. Hu, S. A. Kivelson, Phys. Rev. B **77**, 224509(2008).

[26] C. Xu, M. Muller, S. Sachdev, Phys. Rev. B **78**, 020501(R)(2008).

[27] D. J. Singh, M. H. Du, Phys. Rev. Lett. **100**, 237003(2008).

[28] I. I. Mazin, D. J. Singh, M. D. Johannes, M. H. Du, Phys. Rev. Lett. **101**, 057003(2008).

[29] H. -J. Zhang et al., arXiv:0803.4487(2008).

[30] S. Raghu, X. L. Qi, C. X. Liu, D. J. Scalapino, S. C. Zhang, Phys. Rev. B **77**, 220503(R)(2008).

[31] P. A. Lee et al., arXiv:0804.1739(2008).

[32] R. H. Taylor, Advances in Physics **24**, 681-791(1975).

[33] S. E. Barnes Advances in Physics **30**, 801-938(1981).

[34] A. Shengelaya, G. M. Zhao, H. Keller, K. A. Muller, Phys. Rev. Lett. **77**, 5296-5299(1996).

[35] B. I. Kochelaev, J. Sichelschmidt, B. Elschner, W. Lemor, A. Loidl, Phys. Rev. Lett. **79**, 4274-4277(1997).

[36] Y. Kohama, Y. Kamihara, M. Hirano, H. Kawaji, T. Atake, H. Hosono, Phys. Rev. B **78**, 020512(R)(2008).

[37] G. M. Zhang et al., arXiv:0809.3874v2(2008).